

## TRACE IMPURITIES IN COAL

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### Introduction

As trace impurities in the environment become of increasing concern, those materials that can have important impact on the environment are coming under careful scrutiny. Coal, along with the other sources of energy, is a material of major interest. The Federal Environmental Protection Agency is developing a growing list of environmental contaminants that will have to be monitored in the energy sources. These include mercury, beryllium and asbestos presently, but other elements that have undesirable physiological effects on plant and animal life such as cadmium, arsenic, lead and fluorine will receive increasing attention.

The determination of potentially toxic elements in coal has received little effort in the past. In many cases early information was unreliable because of poor methodology. Coal is a complex material containing both organic and inorganic phases and analyses in the past have suffered from both losses and contaminations in dissolution. Beyond the elemental analysis, the determination of elemental form, whether inorganic or organically bound, will condition the environmental impact. The investigators in the determination of mercury in coal have experienced all these problems in attempting to follow the mass balance of mercury in the combustion of coal.

This paper is still only concerned with elemental analyses. However, methods were investigated for most elements that could be potential environmental pollutants.

Two different general analytical techniques were employed: mass spectrometry and wet chemical methods. Six elements were determined by mass spectrometry and seventeen elements were determined by a variety of wet chemical methods.

### Trace Elements by Spark Source Mass Spectrometry

The spark source mass spectrometric (SSMS) technique is one of the most sensitive instrumental methods for determining inorganic impurities in a variety of materials.<sup>1</sup> Since the advent of electrical detection, this method has become much more rapid and reliable<sup>2</sup>. A method has been developed for the determination of six elements of toxicological interest and correlation between these impurities in the original coal and the coal ash will be shown. Since no primary standards are available at this time for coal, all mass spectrometric data is compared to atomic absorption spectrophotometry (AAS) values determined on the same samples. Relative standard deviations are on the order of 6 to 15% for the mass spectrometric data and 2 to 3% for the atomic absorption values.

### Experimental

An AEI MS-7 spark source mass spectrometer equipped with electrical detection was used in this study. A description of this apparatus complete with manufacturer's accessories and modifications has been described previously and will not be detailed here<sup>2</sup>. The instrument was used in the peak-switching mode only to provide more precise analyses. The instrument operating parameters are given in Table I. The integrated multiplier current for each preset position on the peak switches (each position corresponding to a different isotope to be determined) was displayed on a digital voltmeter. These intensity values were then used to calculate the actual concentration.

### Standard and Sample Preparation

Since no primary standards were available at the time of this investigation, AAS was used to provide analyses on several different coals so that they could be used as secondary standards. Representative portions of

each sample and standard were obtained by grinding and splitting. The samples thus obtained (< 100 mesh) were then weighed into porcelain crucibles and placed into a vented cold furnace and the temperature is elevated to 300°C in one-half hour. The temperature was then raised to 550°C for one-half hour and then to 850°C for an additional hour. The crucibles were then removed from the furnace and the ash dry mixed with a glass stirring rod. The crucibles were then returned to the furnace at 850°C without venting until ashing was completed (usually one additional hour). Samples for SSMS were reground with a boron carbide mortar and pestle and diluted with two parts of high purity graphite. The samples with graphite were placed in polystyrene vials with two or three 1/8" diameter polystyrene beads and mixed in a spex mill for twenty minutes. Electrodes were prepared from the powders using the AEI briquetting die and polyethylene slugs.

Once the electrodes had been prepared, they were placed in the source of the instrument using a standardized mounting procedure. Repetitive exposures were then recorded for each element of interest in the standards and unknowns. The concentrations were calculated from the following relationship:

$$\frac{C_x}{C_s} = \frac{I_x}{I_s}$$

where  $C_s$  and  $C_x$  are the concentrations, the subscripts s and x refer to the standard and unknown, respectively:

$I_s$  and  $I_x$  are the intensities (integrated multiplier currents).

### Results and Discussions

One of the questions posed by the dry ashing of coal is whether or not some of the elements may be lost through volatilization during the combustion process. A comparison of wet ashing and dry ashing of some of the elements analyzed in this study is given in Table II. This data is based

solely on atomic absorption analyses. As can be seen from the table, the agreement between the two sets of data is generally very good. This would seem to indicate that none of these particular elements are lost during the dry ashing of coal. This data does not, however, allow one to make this same generalization for all elements since these are the only elements determined by both ashing techniques during this investigation. Kometani, et. al.<sup>3</sup> have indicated that the presence of sulfates prevents the loss of many elements during dry ashing; and since coal contains appreciable amounts of sulfates, this may help to explain the agreement between the two methods of ashing. Vapor pressure data also imply that these metals could possibly be present as oxides or silicates. Since ash contents of the coals studied varied from 5 to 25% according to the geographical location, the standards for the SSMS analysis were chosen so as to coincide with the approximate area from which the actual samples were taken. Table III is a comparison of the AAS and SSMS data obtained on ten different coal samples from three or four different geographical areas. These values are based upon the metal concentration in the whole coal whereas the analysis was performed on the ash. Again, there is generally very good agreement between the two different methods used. This data also shows that hydrocarbon interference is not a problem at these concentration levels. A very volatile element such as mercury could not be analyzed using this method as it has been postulated that it is pumped away during heating caused by the excitation process, depending upon the parameters selected. The validity of SSMS with electrical detection has proven to be an acceptable method of analysis. Another important aspect of this study was the time involved per sample. Sample and standard preparation (including ashing), electrode preparation, instrument preparation (setting peaks), running of ten samples and four standards, data reduction and conversion to concentration in the whole coal required only fifteen hours. This represents 84 separate analyses. This fifteen

hours also includes sample turn-around time and five separate 0.3nC monitor exposures for each element in each sample and standard. The precision data for the SSMS technique is 6 to 15% relative. The detection limits for the elements studied are on the order of 1 to 2 ppmw in the whole coal using the previously mentioned parameters. This is not necessarily the lower limits as such items as exposure (nC), multiplier gain and sample dilution may increase or decrease this level. From the intensity values obtained during this investigation, absolute detection limits ranging between 0.1 and 0.3 ppm by weight with whole coal would be a realistic estimate. These lower values were not actually determined. The average deviation from the AAS results is 29.2%.

#### Trace Elements by Wet Chemical Methods

The determination of trace impurities by wet chemical methods can immediately be separated into two major divisions. First, those elements that can be dry ashed, leached in acid and the analysis completed by conventional AAS. These elements are Li, Be, V, Cr, Mn, Ni, Cu, Zn, Ag, Cd and Pb. Second, those that require specialized techniques.

1. Hg-O<sub>2</sub> bomb combustion followed by flameless AAS.
2. As, Bi and Sb - dry ashing and acid dissolution followed by determination of their hydrides using AAS.<sup>5, 6</sup>
3. Se-combustion and cold trapping<sup>7</sup> followed by determination as its hydride using AAS.
4. F - O<sub>2</sub> bomb combustion<sup>8</sup> followed by specific ion analysis<sup>9</sup>.
5. B - dry ashing followed by Na<sub>2</sub>CO<sub>3</sub> fusion, dissolution in dilute H<sub>2</sub>SO<sub>4</sub>, then followed by colorimetric determination with carminic acid<sup>10</sup>.

### Determination of Li, Be, V, Cr, Mn, Ni, Co, Cu, Zn, Ag, Cd and Pb

Coal samples are prepared and ashed as described in the procedure employed for SSMS. Five gram samples of coal are used. The ash is placed in 100 ml teflon beaker containing 5 ml of HF (conc.) and 15 ml of  $\text{HNO}_3$  (conc). Warm to dissolve the ash, then evaporate the solution just to dryness. Add water and a few drops of  $\text{HNO}_3$ , then transfer to a 100 ml volumetric flask. Make to volume with water and mix. Immediately transfer to a plastic bottle to preserve as a stock solution for the conventional AAS determinations of Li, Be, V, Cr, Mn, Ni, Co, Cu, An, Ag, Cd and Pb.

Samples were also prepared for conventional AAS determination by wet ashing approximately 5.0 grams of coal in a mixture of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

### The Determination of Mercury

A coal sample is decomposed by burning a combustion bomb containing a dilute nitric acid solution under 24 atmospheres of oxygen pressure. After combustion, the bomb washings are diluted to a known volume and mercury is determined by atomic absorption spectrophotometry using a flameless cold vapor technique.

### Procedure

Transfer approximately 1 gram of 60 mesh X O coal to a clean combustion crucible and weigh to the nearest 0.1 milligram. Transfer 10 ml of 10% nitric acid to the bomb, place the crucible in the electrode support of the bomb, and attach the fuse wire. Assemble the bomb and add oxygen to a pressure of 24 atmospheres (gauge). Place the bomb in the calorimeter (a cold water bath in a large stainless steel beaker is also satisfactory) and ignite the sample using appropriate safety precautions ordinarily employed in bomb calorimetry work.

After combustion, the bomb should be left undisturbed for 10 minutes to allow temperature equilibration and the absorption of soluble vapors. Release the pressure slowly and transfer the contents of the bomb (and crucible) to the mercury reduction vessel by washing with 10% nitric acid. Rinse the bomb, electrodes, and crucible thoroughly with several small washings of 10% nitric acid, then dilute the contents of the reduction vessel with 10% nitric acid to a total volume of 50 ml. Proceed with the determination as described under Standardization. Determine the amount of mercury in micrograms and divide by the sample weight in grams to obtain the mercury value in parts per million.

#### Standardization

Add an aliquot of a standard mercury solution to contain 0.1 micrograms of mercury to the mercury reduction flask. Add  $\text{KMnO}_4$  (3%) dropwise until the pink color persists. Adjust the volume to 100 ml, then add in order 5 ml of  $\text{HNO}_3$  (1:2),  $\text{H}_2\text{SO}_4$  (1:1) and hydroxylamine hydrochloride. When the pink color fades, add 5 ml of the  $\text{SnCl}_2$  (10%) and immediately connect into the system. Start the pump which circulates the mercury in the vapor phase through the optical cell in the atomic absorption spectrophotometer with the mercury lamp optimized at 253.7 nm and normal operating conditions as established by the AA instrument manufacturer. Samples are run by taking all or an aliquot from the  $\text{O}_2$  bomb combustion stock solution.

#### The Determination of Arsenic, Antimony and Bismuth

As, Sb and Bi can be determined by AAS after generation and evolution of their hydrides. The hydrides are formed by the reaction of nascent hydrogen generated by magnesium metal in a  $\text{TiCl}_3\text{-HCl}$  solution. A modified Perkin-Elmer High Sensitivity Arsenic-Selenium Sampling System can be used with any atomic absorption spectrophotometer.

Coal samples for the determination of As, Sb and Bi can be ashed by the method previously described for Li, Be, etc. However, the ash should be leached in HF and HCl. Care must be taken in warming not to lose volatile chlorides. If  $\text{HNO}_3$  is used in place of HCl, a mixed KI and  $\text{SnCl}_2$  must be used in place of  $\text{TiCl}_3$  to generate nascent hydrogen; however, the HCl system is preferred.

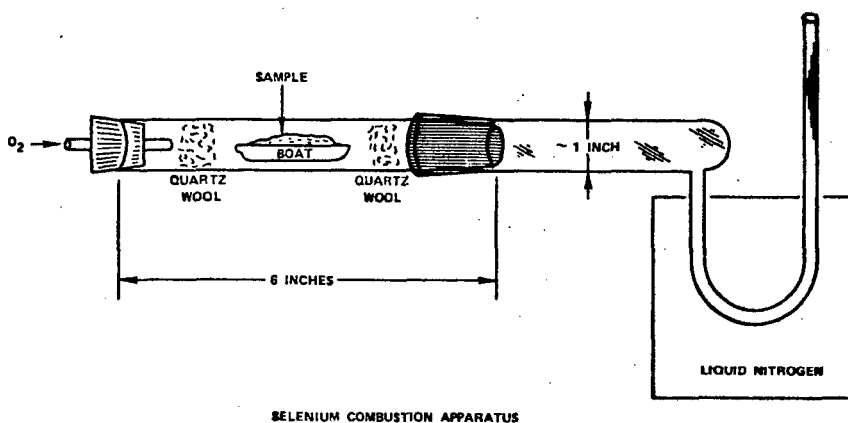
A separate aliquot of HCl-HF sample containing up to 0.3 micrograms of As or up to 0.6 micrograms of Sb or Bi is placed in the hydride generation flask. Add 10 ml of  $\text{TiCl}_3$  (1% in HCl) and adjust the volume to 25 ml with water. After flushing the system with argon for fifteen seconds, add a one inch length of 1/8 inch diameter magnesium rod to the flask through the pinch damp. Allow one minute for collection time in the expansion vessel. Then release gases into the argon-hydrogen entrained air flame using a triple slot-type burner and the AAS manufacturer's standard practices. Blank and appropriate standards are run for each of the elements.

#### The Determination of Selenium

The prior separation of selenium from the bulk of the coal sample uses the combustion technique as described by H. L. Rook<sup>7</sup>. It was originally used in a neutron activation analysis. The equipment was modified to use a quartz combustion tube 5 1/2 inches long connected by a ground glass joint to a second section 3 1/2 inches long. The section ends with a U-tube which can be immersed in a Dewar Flask containing liquid  $\text{N}_2$  or some other suitable coolant. For analyses, an 0.5 gram sample is weighed into a porcelain boat and inserted into the combustion tube with an  $\text{O}_2$  flow of  $\sim 30$  cc/min. With the cold trap in place, the sample is ignited by heating the combustion tube with a meker burner. The coal sample is allowed to burn freely, the temperature is then raised to the maximum of the burner for five minutes. The combustion tube is cooled for five minutes and separated from the condenser section. The condenser is removed from the cold trap and allowed to warm to ambient



temperature. Add 10 ml of HCl to the condenser and flush into a 50 ml volumetric flask. Wash condenser with water and add rinsings to the volumetric flask. Make to volume with water and mix. Take an aliquot of 15 ml or less containing up to 0.3 micrograms of Se and proceed as in the method for As, Sb, and Bi by AAS as previously described.



#### The Determination of Fluorine

A coal sample is decomposed by ignition in a combustion bomb containing  $\text{Na}_3\text{CO}_3$  solution under 24 atmospheres of oxygen pressure. After combustion, the bomb washings are diluted to a known volume and an aliquot is taken to determine F by the standard Orion specific ion procedure.

Transfer approximately 1 gram of coal to a combustion crucible and weigh to nearest 1.0 mg. Transfer 5 ml of  $\text{Na}_2\text{CO}_3$  solution (5%) to the bomb, place crucible in the electrode support and attach the fuse wire. Assemble the bomb and add oxygen to a pressure of 24 atmos. Place the bomb in a cold water

bath and ignite the sample using appropriate safety precautions.

After combustion, the bomb should be left undisturbed for ten minutes to allow temperature equilibration and absorption of the soluble vapors. Release the pressure slowly and transfer contents of the bomb (and crucible) into a 25 ml volumetric flask. Make several small washings with water and add rinsings to the volumetric flask. Make to volume with water and reserve the stock solution in a plastic bottle.

Using an expanded scale pH meter, such as the Orion 801, pipet 10 ml of the stock solution into a small beaker and add 10 ml of Tisab (Orion Cat. No. 94-09-09), determine the electrode potential using a fluoride electrode Orion 94-09. Comparison is made by bracketing with fluoride standards prepared similarly.

#### The Determination of Boron

After dry ashing in the manner used in the Li, Be, etc. procedure, the ash is fused with  $\text{Na}_2\text{CO}_3$ , leached in water and acidified with  $\text{H}_2\text{SO}_4$ . The colorimetric carminic acid method<sup>6</sup> is then used for the determination of boron.

Weigh approximately 1 gram of coal into a platinum crucible and carefully ignite in a vented oven. Gradually increase the temperature to  $850^\circ\text{C}$  and maintain for one hour. Remove from oven and add 2 grams of  $\text{Na}_2\text{CO}_3$  and fuse for ten minutes. Leach in 25 ml of warm water in a teflon beaker. When dissolution is complete, add 10 ml of  $\text{H}_2\text{SO}_4$  carefully. Transfer to a 50 ml volumetric flask. Make to volume with water and reserve in a plastic bottle. Place a 5 ml aliquot or less in a 50 ml volumetric flask, make to 5 ml volume with  $\text{H}_2\text{SO}_4$  (3.6M) if less than 5 ml aliquot was used. Aliquot should contain 0 to 100 micrograms of B. Then add 20 ml of chilled  $\text{H}_2\text{SO}_4$  (18M) and swirl. Then add by pipet 20 ml of carminic acid (0.92 grams in  $\text{H}_2\text{SO}_4$  18M). Make to volume with  $\text{H}_2\text{SO}_4$  (18M) and determine absorbance in 1 cm cells in a spectrophotometer at 605 nm with a reagent blank in the reference cell. Compare to a standard curve containing 0 to 100 micrograms.

TABLE I

## Operating Parameters

Spark Variac	35%
Pulse Repetition Rate (pps)	100
Pulse Length ( $\mu$ sec)	100
Source Slit	0.002"
Multiplier Slit	.002"
Moniter Exposure	0.3nC
Multiplier and Amplifier Gains	Variable according to sample elements and concentration
Electrodes Vibrated	

	Cd
	ASH LEACH
1	2.8
2	0.6
3	13.1
4	0.6
5	<0.5

	Zn
	ASH LEACH
1	121
2	7
3	1420
4	16
5	17

	Ni
	ASH LEACH
1	19
2	4
3	84
4	13
5	7

	Mn
	ASH LEACH
1	67
2	179
3	122
4	12
5	8

	Cu
	ASH LEACH
1	17
2	12
3	50
4	13
5	9

	V
	ASH LEACH
1	55
2	10
3	43
4	18
5	7

	Li
	ASH LEACH
1	68
2	9.5
3	17.1
4	11.8
5	3.1

	Be
	ASH LEACH
1	2.2
2	0.4
3	2.3
4	1.6
5	0.3

	Pb
	ASH LEACH
1	13
2	8
3	105
4	13
5	8

DRY ASHING  
VS  
ACID LEACHING OF COAL

V	
MS	AAS
25	32
21	21
35	23
43	24
24	25
24	21
15	24
20	40
61	37
27	30

Cr	
MS	AAS
26	24
20	12
21	17
12	16
18	19
19	12
13	13
36	31
15	20
37	16

Ni	
MS	AAS
14	23
23	30
21	31
14	21
14	22
28	28
7	15
41	81
7	22
15	18

Mn	
MS	AAS
33	37
7200	193
90	65
101	93
62	52
124	96
11	19
143	117
22	21
73	49

As	
MS	AAS
7.7	7.5
3.2	1.5
6.0	4.5
7.7	4.5
2.4	1.0
9.0	4.0
1.8	3.0
3.8	6.5
8.0	5.0
5.6	1.5

Zn	
MS	AAS
13	9
41	45
17	12
22	24
41	39
84	12
8	13
660	852
18	20
50	36

Cu	
MS	AAS
14	17
23	16
22	18
33	29
11	13
32	29
12	24
38	61
13	14
18	18

TRACE  
ELEMENTS  
IN  
COAL

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